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(54) DYE SENSITIZED SOLAR BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a regeneration dye sensitized solar battery which can be practically used wherein porphyrin derivatives and their metal complexes are usedand which has high photovoltaic conversion characteristics.
SOLUTION: In the solar battery in which an electrolyte is filled between a pair of electrodes wherein a transparent electroconductive film having a porous semiconductor film in an inner side surface is assumed as one side of electrodes and a metal film is assumed as the other side of electrodesand wherein a current circuit is formed between both electrodes by irradiate from the transparent electroconductive film sideat least one kind of pigment selected from porphyrin compounds expressed in a formula (R is hydrogen atom or acid substituted group) and their metal complexes is carried in fine pores of porous semiconductor film.

CLAIMS

[Claim(s)]
[Claim 1]In a solar cell which uses as one electrode a transparent conducting film which has porosity semiconductor membrane in an inner surfaceinserts an electrolyte between electrode pairs which use a metal membrane as an electrode of another sideirradiates with light from the transparent conducting film sideand makes a current circuit form among two polesit is a general formula in fine pores of porosity semiconductor membrane. [Formula 1]

The dye-sensitized solar cell making at least one sort of coloring matter chosen from the porphyrin compounds expressed with (R in a formula is a hydrogen atom or acidic substituent)and those metal complexes support.
[Claim 2]The dye-sensitized solar cell according to claim 1 whose R in a general formula is a carboxyl group.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention has high photoelectric conversion efficiencyand relates to the dye-sensitized solar cell which can supply photoelectric current stable moreover.
[0002]
[Description of the Prior Art]The type which a solar cell is a photoelectric cell with which the purpose of exploiting the energy of sunlight is presentedand is used former most widelyPn junction is made to form near the surface with the large light-receiving surface of a semiconducting crystal or an amorphous boardand the external circuit which irradiates with visible light and connects p field and n field is made to generate current toward n from p. As a semiconducting crystal in this casealthough many silicon is usedthe manufacturing process of silicon is an energy many consumption type intrinsicallyand since harmful silane gas is useda problem is also in respect of environmental protectionand also there is a fault that a manufacturing cost is high.
[0003]By the wayin 1991 gray TSUERU and others of Switzerland (Graezel)The electrode which made the surface of the porosity titanium dioxide thin film with large surface area absorb ruthenium bipyridine carboxylic acid coloring matter is usedSince the dye-sensitized solar

cell was announced and there have been the strong pointssuch as that there is no fear of environmental pollution that a manufacturing cost is cheapand having high photoelectric conversion efficiencya reproduced type dye sensitizing photoelectric conversion cell has come to attract attention. Howeveralthough what the chlorophyll derivativethe zinc complex of porphyrinetc. made the optical-pumping center until now is proposed as this dye-sensitized solar cellthese may be satisfied in order to present practical use as a solar cellsince the photoelectric transfer characteristic is low.

[0004]

[Problem(s) to be Solved by the Invention]This invention is a basis of such a situation and is made for the purpose of providing the utilizable reproduced type dye-sensitized solar cell using the porphyrin derivatives which have a high photoelectric transfer characteristicand those metal complexes.

[0005]

[Means for Solving the Problem]A result of this invention persons having manufactured a metal complex of various porphyrin derivativesand having examined many things about the photosensitization operationNew 510 and 1520 **TETORA phenylporphyrinor its derivativeOr when that metal complex is used as coloring matter of a dye-sensitized solar cellit finds out that a solar cell which shows a high photoelectric transfer characteristic and can supply stable photoelectric current is obtainedand came to make this invention based on this knowledge.

[0006]That isthis invention is a general formula in fine pores of porosity semiconductor membrane in a solar cell which uses as one electrode a transparent conducting film which has porosity semiconductor membrane in an inner surfaceinserts an electrolyte between electrode pairs which use a metal membrane as an electrode of another sideirradiates with light from the transparent conducting film sideand makes a current circuit form among two poles. [Formula 2]

The dye-sensitized solar cell making at least one sort of coloring matter chosen from the porphyrin compounds expressed with (R in a formula is a hydrogen atom or acidic substituent) and those metal complexes support is provided.

[0007]

[Embodiment of the Invention]Nextan embodiment of the invention is described according to an accompanying drawing. Drawing 1 is one example of the structure of this invention solar cell a sectional view for being

shownand between two glass substrates (the transparent substrate 1 and 7for exampleglass substrates)The transparent conducting film 2the porosity semiconductor membrane 3the electrolyte 5and the metal membrane 6 are arranged one by oneand said semiconductor membrane 3 is formed in porosityand adsorption support of the porphyrin compound expressed with said general formula (I) in the fine pores or its metal complex is carried out. 8 is a current circuit and 9 is an ammeter.

[0008]As a material of the above-mentioned transparent electric conductor 2the complex of the tin oxideand it and indium oxide is usedfor example. As a material of the semiconductor membrane 3titanium oxidea zinc oxidetantalum oxideetc. are used. This semiconductor membrane 3 needs to form as porosity. The semiconductor membrane which has such porosity semiconductor membrane on the surfaceFor examplejournal physical chemistry (J. Phys. Chem.)the 94th volumeand the method indicated to 8720 pages (1990) are referred toMelt titanium tetraisopropoxide in the mixture of 2-propanoldeionized waterand nitric acidhydrolyzeand a stable titanium oxide colloidal solution (particle diameter of about 8 nm) is preparedAfter mixing this solution with TiO_2 impalpable powder (the product made by Japanese Aerosila trade name "P-25")and a polyethylene glycol and carrying out spin coating of this mixture on semiconductor membraneit can manufacture by calcinating above 500 **.

[0009]Nextas a material of the metal membrane 6 used as a counter electrodealthough aluminumtinsilvercopperetc. are usedespecially a desirable thing is platinum. This metal membrane 6 can form metal chemical vacuum deposition or by carrying out a physical vapor depositionfor example on a glass substrate and other transparent substrates.

[0010]In this inventionit is required to make at least one sort of coloring matter chosen from the porphyrin compound expressed with said general formula (I) in the fine pores of the aforementioned porosity semiconductor membrane 3 and its metal complex support. As a metal complex of this porphyrin compoundit is a general formulafor example.

[Formula 3]

The metal complex expressed with (a hydrogen atom or acidic substituentat least one sort of ligands as which X is chosen from an alkoxy groupan aryloxy groupan acyloxy groupand a halogen atomand M of R in a formula are MoCrNbor W) can be mentioned. General formula HX' (III) after making the carbonyl compound of MoCrNbor W react to the porphyrin

compound which the metal complex expressed with this general formula (II) is a new molecular entity of literature non-**for exampleis expressed with said general formula (I)or its derivative
It can manufacture by processing with a compound expressed with (X' in a formula is an alkoxy groupan aryloxy groupan acyloxy groupor a halogen atom)and processing by hydrogen halide further according to a request.
[0011]Although R in a porphyrin compound which is this general formula (I) or (II)and is expressedor its metal complex is a hydrogen atom or acidic substituentas this acidic substituentthere are a carboxyl groupsulfonic acid residuesulfonate residuesulfuric acid residuesulfate residueetc. for example. M is a metal atom which can form porphyrin and a complexi. e. MoCrNbor W.
[0012]X is a basis used as a ligand of Mand Nexta methoxy groupan ethoxy basisa propoxy groupThere are an acyloxy group like an alkoxy group like a butoxy groupa phenoxy groupan aryloxy group like p **MECHIRU phenoxy groupan acetyloxy groupa propionyloxy groupand a glycyl oxy groupa fluorine atoma chlorine atoma halogen atom like a bromine atometc.
[0013]A metal complex of a porphyrin compound expressed with said general formula (II)To a porphyrin compound like 5101520 **TETORA phenylporphyrin or 510 and 15and 20 **TETORA substituted phenyl porphyrinmetal carbonylFor examplemolybdenumhexacarbonylchromiumpentacarbonylniobiumpentacarbonylAfter making tungstenpentacarbonyl etc. reactit can manufacture easily by making alcoholphenoland carboxylic acid contactcontacting the output to hydrogen halide according to a request furtherand crystallizing. A reaction of this porphyrin compound and metal carbonyl can be performed using a solventfor exampledimethylformamideaccording to a request. This reaction is advantageous at a point that go on in a short time of 30 minutes thru/or 2 hours in a room temperaturea porphyrin metal complex is obtained with high yield of not less than 65%and moreover refining is also easy.
[0014]In order to make the porosity semiconductor membrane 3 support at least one sort of coloring matter 4 chosen from a porphyrin compound which is general formula (I) or (II) and is expressedand its metal complexAfter neglecting it until it dissolves this coloring matter in a suitable solventfor exampledimethylformamideit carries out the dipping of the porosity semiconductor membrane into this solution and coloring matter fully adsorbs into fine pores of porosity semiconductor membranethis is taken out and it dries after washing if needed.
[0015]Nextin this invention solar cellalthough platinum is preferred as a material of the metal membrane 6 used as a counter electrodea thing

publicly known as a counter electrode of the conventional solar cellssuch as the other aluminumsilvertinand indiumcan also be used arbitrarily. As for these metal membranes 6it is preferred to form a physical vapor deposition or by carrying out chemical vacuum deposition on a glass substrateor indium oxide and a tin-oxide complex board.
[0016]In this invention solar cellas an electrolyte inserted between two electrodesalthough conventionally used as an electrolyte of a solar cellit can choose from inside suitably and can use. An electrolyte used as such a thing with a solar cell using ruthenium bipyridine carboxylic acid coloring matter of gray TSUERU and others mentioned abovefor exampleThat isthere are some which dissolved iodine and potassium iodide in a medium which consists of a mixture of polypropylene carbonate 25 mass % and ethylene carbonate 75 mass %.
[0017]Thickness of the transparent conducting film 2 in this invention solar cell 0.4-0.6 micrometerAs for the particle sizethickness of 0.01-0.03 micrometer and the metal membrane 6 is chosen in 10-15 micrometers inand 5-30 micrometers of thickness [0.01-0.06 micrometer of / 2-20 micrometers of] of 0.5 micrometer and the porosity semiconductor membrane 3 are preferably chosen in 10-12 micrometers. A range of 8-20 micrometers of thickness of an electrolyte inserted between two electrodes is 10-12 micrometers preferably.
[0018]If a solar cell of such a structure connects between two electrodes with a leadand makes a current circuit form and it irradiates with 420-nm white light from the transparent conducting film sideit can be generated with high photoelectric conversion efficiency of not less than 2.9%. Since this photoelectric conversion efficiency is influenced by thickness of each filma state of semiconductor membranethe amount of adsorption of coloring matterelectrolytic kindetc.it can be further raised by choosing these optimal conditions.
[0019]
[Example]Nextan example explains this invention still in detail.
[0020]The mixture of the reference examples 1510and 150.5 g (0.6mmol) of 20 **TETORA (4 **KARUBOKISHI phenyl) porphyrin0.8 g (3.2mmol) of molybdenumhexacarbonyland 100 ml of dry dimethylformamide was refluxed under a nitrogen atmosphere for 2 hours. The stages of progress of the reaction were pursued with the ultraviolet visible spectrum in the meantime. Subsequentlythe solvent was distilled offafter suspending heating and cooling a reaction mixture radiationally to a room temperature. Subsequentlythe glossy crystal was obtained with the yield of 67% by recrystallizing the solid of dark green obtained by carrying out ionic exchange column chromatography processingand refining a

residue in ethyl alcohol. An ultraviolet visible spectruman infrared absorption spectrumESRultimate analysisand when mass-spectrum analysis was conductedit was checked that it is a porphyrin metal complex (D) in which X in said general formula (II) corresponds to an ethoxy basis about this crystalM corresponds to Moand R corresponds to the structure of a hydrogen atom. It processes similarlyusing 5101520 **TETORA phenylporphyrin or 510 and 15and 20 **TETORA (4 **SURUHO phenyl) porphyrin as a raw materialThe porphyrin metal complex (E) and (F) in which X in said general formula (II) corresponds to an ethoxy basisM corresponds to Moand R corresponds to the structure of a carboxyl group or a sulfonic group was obtained.

[0021]Into 60 ml of hexane which saturated reference example 2 hydrogen chloridethe solution which melted 50 ml of porphyrin metal complexes (E) obtained by the reference example 1 in 15 ml of ethyl alcohol was dropped at the room temperature. The generated crystal was ****(ed) with the glass filter and white crystals were obtained with the yield of 82% by drying after washing by hexane. It was checked that it is a porphyrin metal complex in which X [in / for this thing / said general formula (II)] corresponds to a chlorine atom an ultraviolet visible spectruman infrared absorption spectrumESRultimate analysisand when mass-spectrum analysis is conductedM corresponds to Moand R corresponds to the structure of a carboxyl group.

[0022]Instead of the molybdenumhexacarbonyl in the reference example 3 reference example 1chromiumhexacarbonylWhen it was made to react similarly using niobium hexacarbonyl or tungstenhexacarbonylthe porphyrin metal complex in which CrNbor W corresponds [M in general formula (II)]respectively was obtained.

[0023]After dissolving 62.5 ml of example 1 titanium tetraisopropoxide into 10 ml of 2-propanoland the mixture of 380 ml of deionized waterand 3 ml of concentration 70 mass % nitric acid and making it hydrolyze in 80 ** for 8 hoursevaporation concentration was carried out and the stable titanium oxide colloidal solution was prepared. The particle diameter of this titanium oxide was about 8 nm. As a result of carrying out an X diffractionit turned out that this titanium oxide is an anatase type. On the surface of the sheet metal (25x25 nm) of a 0.5-micrometer-thick indium oxide tin-oxide complex (henceforth [ITO]). The 10-micrometer-thick porous-titanium-oxide film was made to form by carrying out spin coating of the aforementioned colloidal solution 10gand 2 g of TiO_2 impalpable powder (the product made by Japanese Aerosila trade name "P-25") and a mixture with 2 g of polyethylene glycolsand calcinating them at 500 ** for 1 hour.

[0024]5101520 **TETORA phenylporphyrin (A)510 and 1520 **TETORA (4 **KARUBOKISHI phenyl) porphyrin (B)5101520 **TETORA (4 **SURUHO phenyl) porphyrin (C)5101520 **TETORA phenylporphyrin metal complex (D) which were obtained by the reference example 15101520 **TETORA (4 **KARUBOKISHI phenyl) porphyrin metal complex (E) and 510 and 15and 20 **TETORA (4 **SURUHO phenyl) porphyrin metal complex (F) are dissolved in dimethylformamide with $5x10^{-4}$ molar concentration. After carrying out the dipping of the above-mentioned porous-titanium-oxide film into the prepared solution and neglecting it in 80 ** overnightit took out in argon atmosphereand washed and dried with methyl alcohol.
[0025]As a counter electrodeusing what provided platinum membrane (10 micrometers in thickness) by sputtering process on the ITO board (22x25 mm) as an electrolyteThe solar cell of the structure which shows the iodine 0.38g and the mixture of 2.49 g of potassium iodide in drawing 1 using what was dissolved in the mixture 30g of propylene carbonate 25 mass % and ethylene carbonate 75 mass % was manufactured. Before longthe performance of the solar cell of B and C was as follows.
[0026]
[Table 1]

[0027]
[Effect of the Invention]The dye-sensitized solar cell which can supply the photoelectric current which has high photoelectric conversion efficiency and was moreover stabilized by this invention is provided.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1]The sectional view showing one example of the structure of the solar cell of this invention.
[Description of Notations]
1 and 7 Transparent substrate
2 Transparent conducting film
3 Porosity semiconductor membrane
4 Coloring matter
5 Electrolyte
6 Metal membrane
8 Current circuit

9 Ammeter